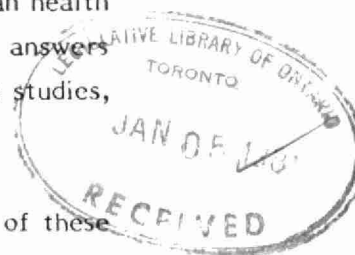## WHAT'S A MILLION?

C. D. Howe, Minister of Defence in Canada's wartime cabinet, is remembered for his famous one-liner "What's a million?" Mr. Howe was dealing in dollars, and people quickly related to the significance of his statement.

Environmentalists, polluters, government regulatory officials, and the public at large, are daily inundated with information on pollution levels in the parts per million or parts per trillion concentration. Unlike the instant insight provided by C. D. Howe's cryptic comment, very few people can relate to or comprehend the significance of these numbers. In terms of human health, very little is known concerning the short or long term effects of exposure to trace concentrations of pollutants.

Advances in analytical technology have provided us with the tools to measure infinitesimally small quantities of substances whose environmental or human health significance is unknown. There is little relief in sight in terms of medical answers to these questions, due in part to the high cost of mounting health effect studies, and the horrendously large number of chemicals which need to be tested.

There is an urgent need to develop a means of assessing the relative risk of these substances in the absence of hard scientific data. Currently a "language of distress" surrounds the discussion of environmental pollutants; substances are touted as being potential carcinogens, teratogens, or mutagens, based on animal studies in which quite large doses of the substance in question were fed to the animals. The reader is usually left with the impression that humans will be similarly affected by exposure to the trace levels of these compounds present in the environment. The problem is further compounded by the reported presence of a never-ending stream of complex chemicals in the food we eat, the air we breathe, the water we drink, the land we till, with no hint as to their environmental or human health significance.

The scientific tools now available have enabled us to be more knowledgeable than ever before on environmental matters. There are many complex environmental health issues, however, for which there are no readily available answers. While

acknowledging the many challenging issues which must be addressed in Ontario, these must be considered in the context of a widely acclaimed record of solid achievement in environmental protection.

We live longer, we live better in material terms, and we are more aware of what needs to be done to protect our environment, than any other generation of humans. There is a happy balance between a Pollyanna view and a gloom and doom perspective. The "language of distress" must be tempered by a "language of optimism" to better reflect the real world in which we live.

## LOCALIZATION OF LEAD IN PLANT TISSUES BY TRANSMISSION ELECTRON MICROSCOPY

Accumulation of heavy metals in vegetation has been frequently found in the vicinity of primary and secondary smelting operations, highways and other emission sources of atmospheric particulate pollution. During the past few years, lead uptake and localization in plant tissue has been under investigation by the Phytotoxicology Section, Air Resources Branch. Initial studies were conducted using specific staining techniques, with examination under an optical light microscope. Since lead is known to be electron dense (the electron beam is absorbed) when observed under an electron microscope, localization of lead in plant tissues at the ultrastructural level is feasible. Electron microscopic studies of plant tissues were made, using the facilities and technical assistance of the Laboratory Services Branch.

Corn and radish seedlings were grown in the phytotoxicology laboratory, in solutions containing 40 ppm lead at pH 4.5, for a period of two weeks. The seedlings were harvested, washed carefully in distilled water and fixed in 2.5% glutaraldehyde in 0.5 M phosphate buffer at pH 7.0, and 1% osmium buffered solution. Samples were dehydrated by serial immersions in alcohol-water mixtures, then in propylene oxide, and the dehydrated material was embedded in araldite-epoxy plastic resin. Sections were cut by means of an LKB 111 ultramicrotome and stained with alcoholic uranyl acetate to enhance contrast.

For obvious reasons, sections were not counter-stained with any lead-containing reagent, as is the usual procedure for biological sampling staining prior to viewing under transmission electron microscope.

Preliminary results showed that lead was taken into the root tissue from the external lead source. Large amounts of lead were observed in the root tip region. The lead deposits, spherical or irregular in shape but of varying sizes, were observed mainly in the intercellular space, mixed with the middle lamella substances or the primary cell walls of cortical parenchymatous cells (Figures 1, 2). In cytoplasm of young living cells, spherical lead deposits were not found, but there was an increase in electron density of total organelles and stromatic substances within the cell, as compared to controls. This suggests that the cytoplasmic membranes are permeable to lead, and diffusion into the cytoplasm from cell walls can take place. In the old root cells, where degradation of cell contents was occurring, electron dense deposits of various sizes containing lead were often found in the cell lumens and in the vacuoles. The tonoplast (vacuolar membrane) was particularly darkened in color. A further increase in electron density was observed in the dead shrunken cell debris after cell degeneration (Figure 3).

Lead was transported from the root into the stem and leaf tissues. Highly electron dense substances were observed both along the tonoplast and deposited within the membrane in some leaf parenchymatous cells and epidermal cells (Figure 4). Other membranes such as the chloroplast envelope, the plasmalemma (cytoplasmic membrane) and the mitochondria envelope were darker than those from untreated control samples. In some young xyleme lumens and other vascular bundle cells, heavy electron dense depostis lining the inner cell walls or in the cell lumens were seen also. To confirm these findings in leaf tissues, further studies are in progress using a scanning electron microscope, equipped with wavelength and energy-dispersive X-ray spectrometers.
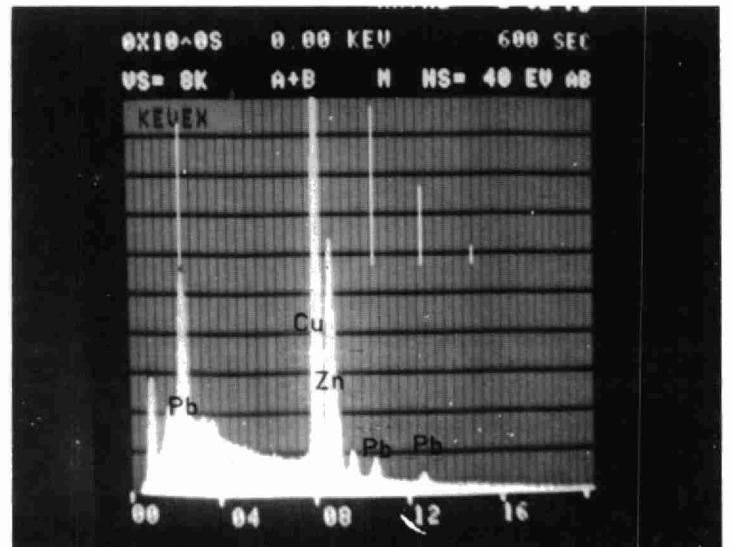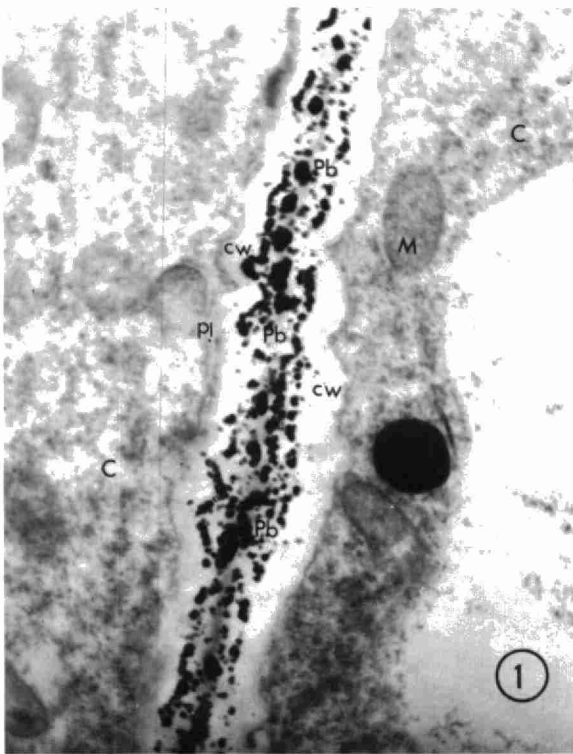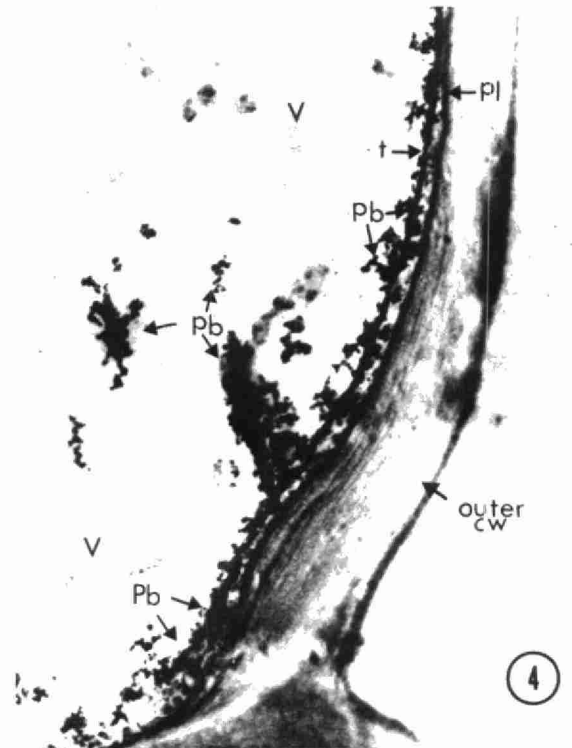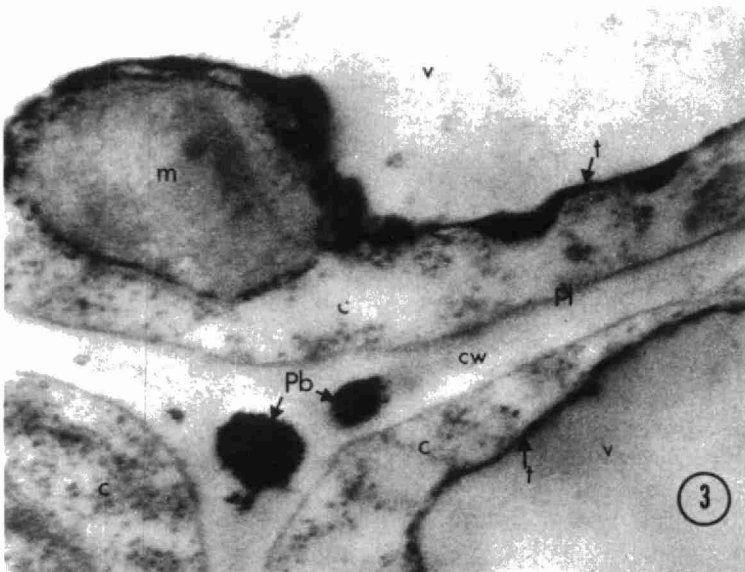
Electron micrographs of corn seedlings grown in Knop's solution containing lead for two weeks. Lead deposits were observed in the intercellular space of root tip cortical cells (Fig.1, X20,000), which were further confirmed by the energy dispersive X-ray spectrometer (Fig. 2). Electron dense deposits were also observed in the vacuole and on the tonoplast in root(Fig.3, X46,000); and in .the epidermal cell of leaf tissue(Fig. 4, X16,000).

lead deposts(pb), cell wall(cw), cytoplasm(c), mitochondia(m), plasmalamma(pl), tonoplast(t) and vacuole(v).

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POLYNUCLEAR AROMATIC HYDROCARBONS IN RESPIRABLE AIR-BORNE DUST

The air we breathe contains solid particles from both natural and man-made sources. Although they consist primarily of inorganic materials such as silica, hematite and other mineral dusts, they may also contain a wide variety of organic compounds resulting from the combustion of carbonaceous materials. Thus, smoke emissions from giant coke ovens, such as those used by steel mills, have been found to contain high levels of polynuclear aromatic hydrocarbons (PAH). Since some of these compounds are potent carcinogens, it is essential that we determine how much PAH is associated with the sizes of particles most likely to reach the lungs.

ANDERSEN SAMPLERS –
Simulates Human
Respiratory System
PRESEPARATOR
10 micrometers and above

STAGE 0 9.0–10	
STAGE 1 5.8.–9.0	
STAGE 2 4.7–5.8	pharynx
STAGE 3 3.3–4.7	trachea & primary bronchi
STAGE 4 2.1–3.3	secondary bronchi
STAGE 5 1.1–2.1	terminal bronchi
STAGE 6 0.65–1.1	alveoli
STAGE 7 0.43–0.65	alveoli

ANDERSEN SAMPLER SIMULATES
HUMAN RESPIRATORY SYSTEM.

In cooperation with regional staff, the Laboratory Services Branch has undertaken an investigation into the distribution of PAH compounds over the range of particle sizes found in total suspended particulates (TSP). Fractionation of TSP is achieved by the use of a sampling device known as the Andersen Impactor. It is designed to separate and collect air particulates according to their size range and, as shown in the Figure, closely simulates the human respiratory system in its capability to filter out particles. The respirable particulates smaller than about 5.5 micrometer (uM), which are capable of passing through to the bronchi and the lungs, are of greatest concern.

In this study, air particulate matter in the vicinity of the steel mills located in Hamilton and Sault Ste. Marie was subjected to size fractionation by means of the Andersen Impactor. The particle fractions from the various filtration stages were analyzed separately for a number of PAH compounds and it was found that approximately 80-90% of PAH are associated with respirable particles.

These findings provide a clearer understanding of the significance of the levels of PAH observed during the routine air quality monitoring surveys carried out in many municipalities across Ontario.

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ELIMINATION OF CHEMICAL INTERFERENCES IN THE HYDRIDE METHOD FOR SELENIUM

Analytical methods based on the generation of volatile hydrides followed by atomic absorption spectrophotometric measurement have become very popular for the determination of selenium, arsenic and other related elements. The spectrophotometric methods are often subject to spectral interferences, while volatile hydride formation is subject to chemical interferences. Literature references cite severe interference by ions of Ag, Cu, Ni, Pd, Pt, Rh, Ru, Sn and a moderate degree of interference by Au, As, Cd, Co, Fe, Ge, Pb, Zn. Earlier work in the MOE laboratory had minimized this problem by coprecipitation of selenium with manganese dioxide in an acid medium, leaving heavy metal ions in solution. However, the method was somewhat tedious and time consuming. Complete recovery of 50 ng Se/ml was obtained from test solutions containing 10 ug/ml each of Cu, Ni, Fe, Pb and Sn.

More recent studies have indicated that not only can the interference by the most common heavy metal ions be effectively suppressed by the formation of their stable chloro-complexes with hydrochloric acid, but the differentiation between hexavalent and tetravalent selenium can be achieved by analyzing the sample solutions prepared in 1N and 9N HCl media. To study the role of HCl in complexation and speciation, the following test solutions were prepared:

Complexation:

1. 20 ng/ml Se^{4+} and 50 ug/ml Cu^{2+} in 0-10N HCl.

2. 20 ng/ml Se^{4+} and variable concentrations of interfering ions, prepared in 9N HCl.

3. digestates of NBS and EPA reference material samples containing added amounts of variable concentrations of heavy metals.

Speciation

1. Composite solutions of Se^{4+} and Se^{6+}, containing 0-20 ng/ml of each, prepared in 1N and 9N HCl.

2. 20 ng/ml Se^{6+} prepared in 1-12N HCl.

The above solutions were analysed using an automated hydride - AAS system. The results of the tests showed that when the HCl concentration exceeded 6N, there was no interference by the metal ions added. Nitric and perchloric acids did not produce the same effect because of their inability to complex heavy metals. Apart from acting as a complexing agent, hydrochloric acid also provides the hydrogen ions required for the chemical reaction with sodium borohydride. It was observed, however, that greater than 8N HCl caused a significant decrease in the selenium signal. The optimum HCl concentration for maximum sensitivity and freedom from heavy metal interference was found to be between 6N and 8N. Hydrochloric acid was also found to be an effective reducing agent at concentrations greater than 5N HCl, converting Se^{6+} to Se^{4+}. At lower concentrations, no such reduction took place. This provided a means of differentiating between the two species. Samples prepared in 9N HCl were analyzed for total selenium and those prepared in 1N HCl were analyzed for Se^{4+}. The speciation results obtained on artificial standards are shown in Table I. Table II contains the results of analyses of reference samples containing added amounts of copper, nickel and iron as interferents.

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TABLE I

Speciation Results

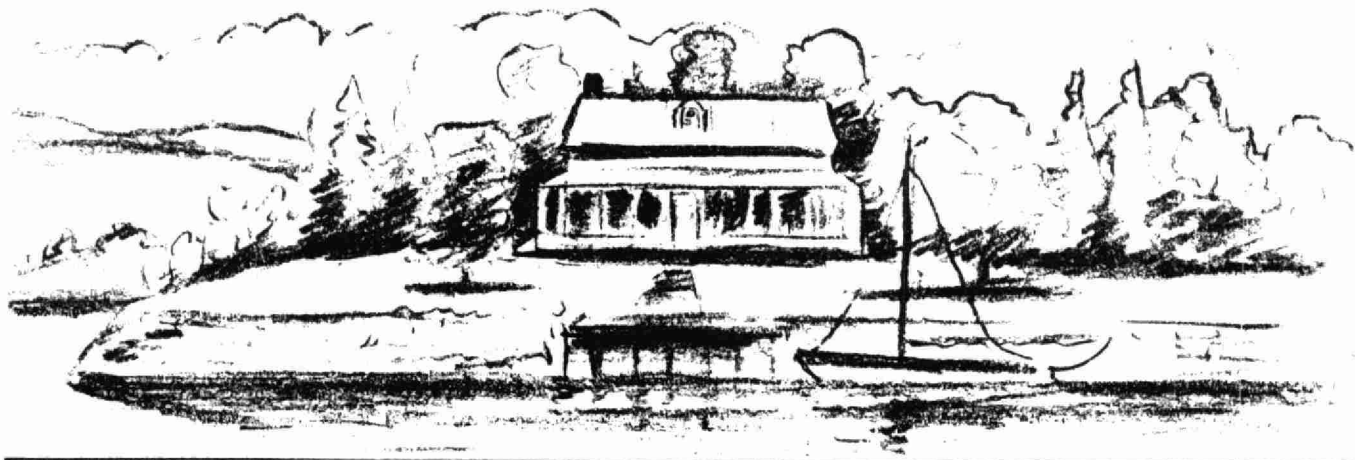| Selenium added (ng ml^{-1})			Selenium found (ng ml^{-1})		
Se^{+4}	Se^{+6}		Se^{+4}	Total Se	Se^{+6}
0	20		0.1	20.1	20.6
4	16		3.9	20.4	16.5
8	12		7.8	20.2	12.4
12	8		12.2	19.9	7.7
16	4		16.0	20.2	4.2
20	0		19.8	20.0	0.2

TABLE II

Analysis of Reference Samples
Spiked[a] with Interferents

Sample	Se found[b] ug g^{-1}	Certified Value ug g^{-1}	% Recovery
Albacore Tuna #SRM 50	3.84 ± 0.10	3.96 ± 0.2	97%
Bovine Liver #SRM 1577	1.05 ± 0.05	1.10 ± 0.1	95%
Wheat Flour #SRM 1567	1.00 ± 0.10	1.10 ± 0.2	92%
Rice Flour #SRM 1568	0.38 ± 0.05	0.40 ± 0.1	95%
EPA #1	8.8 ng ml^{-1}	8.7 ng ml^{-1}	101%
EPA #2	24.1 ng ml^{-1}	24.0	100.4%
EPA #3	16.0 ng ml^{-1}	16	100%

a) Sample solutions spiked with 10, 25, 25 ppm of Cu^{+2}, Ni^{+3}, Fe^{+3}, respectively.

b) Mean of triplicate analyses.

DISSOLVED INORGANIC CARBON ANALYSIS AT LOW PPM LEVELS

Samples submitted for analysis in conjunction with the Acid Precipitation Study in Ontario often require the analysis of low levels of dissolved inorganic carbon (DIC). A Technicon AutoAnalyser system was modified to provide two channels for simultaneous DIC analysis, with full-scale calibration ranges of 2 mg/L and 10 mg/L of carbon. The higher range is used to study background DIC levels in lakes in the Dorset area, whereas the lower range is used for background level and for primary productivity studies.

Primary productivity is the process of fixation of atmospheric carbon dioxide into organic carbon. In soft water shield lakes, measurement of the uptake of inorganic carbon is the most sensitive method of measuring the rate of accumulation of organic matter. Primary productivity can be used to estimate trophic levels and fish productivity. Reduced primary productivity may result if DIC levels fall below 0.05 mg/L C.

Dissolved inorganic carbon plus carbon dioxide is measured by converting any carbonate and bicarbonate species present to carbon dioxide by acidification to pH 2. The sample is heated to lower the solubility of the CO_2 and the sample is then passed over two gas permeable dialysis membranes connected in series. The CO_2 passes through the membranes and is absorbed into a weakly buffered alkaline solution containing borate, bicarbonate and phenolphthalein indicator. As the carbon dioxide is absorbed, the pH of the buffer solution as well as the colour of the phenolphthalein indicator decreases. The decrease in absorbance is monitored by a Technicon AAII colorimeter operating in the inverse mode.

Modifications to the current method include insertion of a heating bath maintained at 60°C and a second 15 cm long dialyser. Peak height increased fairly linearly with temperature at a rate of 1.7 mm per °C. Addition of the second dialyser resulted in an increase of 85% in the slope of the calibration curve.

The 2.0 mg/L C range was linear but showed a small variable blank. The precision, as estimated from the standard deviation of duplicate analyses of routine samples, ranged from 0.01 to 0.07 mg/LC depending on sample concentration. The calibration curve for the 10.0 mg/L C range was linear below 2.0 mg/L C but was curved in the upper regions. The standard deviation for duplicate analyses of samples between 2.0 and 5.0 mg/L C was 0.061 mg/L C.

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AIR PARTICULATE MATTER FRACTIONATION WITH THE DICHOTOMOUS SAMPLER

The traditional method for sampling suspended air particulate matter has been with the "high volume" air sampler. This sampler consists of a simple vacuum cleaner motor which draws air through a preweighed 20 cm x 25 cm glass fibre filter. After sampling the filter is weighed again and the total particulate loading can be calculated and related to the air volume drawn through the filter. The design of the sampler is such that at an air flow rate of 60 cubic feet per minute, only particles of less than 100 um diameter aerodynamic size will be collected.

For several years, researchers have believed that the particles of greatest health concern were in the < 3 um diameter size range, because these particles could penetrate deep into the lungs. New evidence indicates that particles that are deposited in the upper part of the lungs can also have deleterious human health effects. These particles are generally in the 3 um-15 um diameter size range.

The USEPA is currently considering setting ambient air standards for "inhalable particles" (IP). However, before such standards are set, a data base is required on the concentration of IP in ambient air. For this purpose, a new type of air sampler was designed by the Lawrence Berkeley Laboratory of the University of California under contract to the EPA. Commercial versions of the sampler have been available in Canada for about two years.

The sampler operates in the following manner (Fig. 1). Air is drawn into the sampler at a flow rate of one cubic meter an hour. The sampler inlet is so designed that under normal wind speeds, only particles less than 15 um in diameter can enter the sampler. The airstream carrying the particles is then divided into two segments, containing different sized particles. The particles from each segment are collected on a separate filter.

The particle size separation is achieved by impinging the initial aerosol flow against the entrance to a collection nozzle, thus causing particles with a diameter greater than 2.5 um to enter a collection chamber which is constantly evacuated. Particles with a diameter smaller than 2.5 um, because of their aerodynamic mobility, are swept to a second nozzle of smaller diameter and are also collected on a suitable filter. From this split in sampled particulate size ranges is derived the name of the sampler, i.e. the dichotomous sampler.

Since the dust is collected on chemically pure filter material such as teflon, trace metal analysis on the material is possible. The method of choice at the moment is energy dispersive x-ray fluorescence spectrometry, because of its speed and non-destructive nature. However, this system as used at EPA's Research Triangle Park facility, is not capable of analyzing any type of sample except for dichotomous samples. Because of this inflexibility and questions concerning transportation of samples, relationship between human respiratory functions and filter cut-off points, the Air Resources Branch, Laboratory Services Branch and Central Region had been investigating these filters and various analytical methods for the past year.

The study, initiated to thoroughly test all aspects of the dichotomous samples program includes:

- an investigation of various filter media,

- determination of cut-off points,

- problems in transportation and handling of filters,

- methods of determining accurate loadings for the extremely small masses of particulates sampled,

- development of sensitive techniques for chemical analysis of particulate matter collected on the filters. Techniques being studied in the LSB include flameless atomic absorption spectrometry, inductively coupled plasma emission

spectrometry, and wavelength dispersive x-ray fluorescence.

Modification of the instrument to more closely resemble human respiratory functions is also being considered. Furthermore, the Federal Government is planning a nation-wide survey using dichotomous samplers. Within the Ontario Ministry of the Environment, the Air Resources Branch, the Central Region and the Laboratory Services Branch are active participants in this survey.
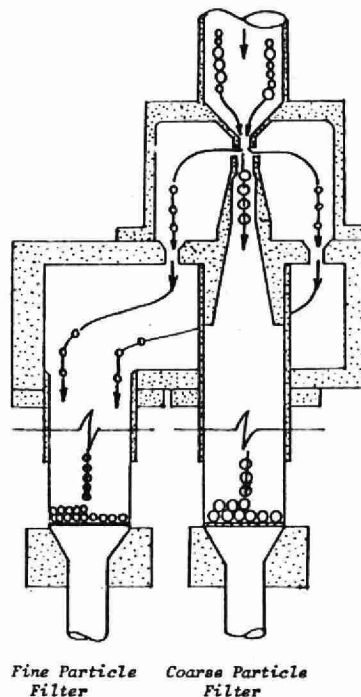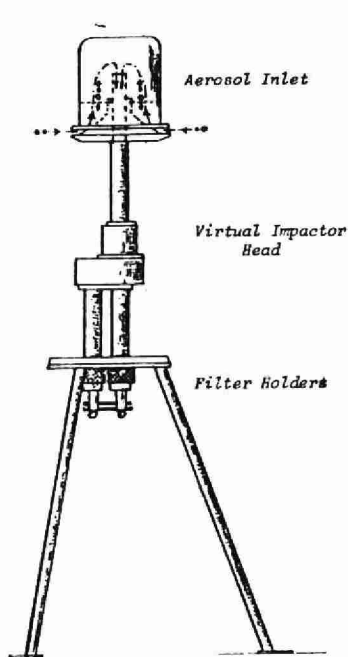
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FIG. 1   Dichotmous Air Sampling Module and Virtual Impactor Head.

A CONCENTRATION TECHNIQUE FOR VOLATILE MUTAGENS IN ENVIRONMENTAL SAMPLES

With the advent of short-term mutagenicity tests, much attention has focused recently on the identification and control of mutagenic /carcinogenic contaminants in drinking water. There has been less emphasis placed on the environmental health effects associated with industrial effluents. It has been determined using the simple bacterial test developed by Ames, that about 90 percent of organic chemical carcinogens are mutagens. In order to monitor industrial effluents for mutagenicity by this and other short-term bacterial assays, it was advantageous to devise a concentration technique compatible with such tests and involving minimal loss of organics. Concentration methods published to date have been designed primarily for the nonvolatile components of aqueous and air samples. This paper describes the development of a simple, inexpensive and rapid procedure for concentration of volatile organics from aqueous effluents. The concentrates obtained are suitable for direct testing by the bacterial assays of Ames or Rosenkranz.

The method is based on the principle of purging the volatile organics from solution using an inert gas, and trapping these compounds on an adsorbent. The sample is placed in a one litre vessel and purged at $90^{\circ}C$ with nitrogen at a flow rate of 10 mL/min. Two traps are employed sequentially, using purge times of 30 and 60 minutes respectively. These glass traps have a bed volume of 2.0 mL and are packed with Tenax GC adsorbent. After purging, the traps are each eluted with 1.0 mL dimethylsulphoxide (DMSO), and the eluant is removed by centrifugation. The resulting 2.0 mL concentrate is then ready for mutagenicity testing, DMSO being the solvent of choice for bacterial assays.

The described two-trap procedure evolved as a result of recovery efficiency studies where several parameters were varied to establish the optimal purge trap conditions. Variables included trap size and number, nitrogen flow rate, purge time, eluant volume, and spike concentration. Standards were used throughout the developmental work and chemicals with a wide diversity of functional groups were studied, also taking into consideration volatility and potential mutagenicity.

Once established, the two-trap system was applied to mixtures containing up to nine compounds spiked at concentrations of 2 to 30 mg/L in distilled water. The chemicals studied most intensively were the following: chloroform, 1,2-dichloroethane trichloroethylene, dibromomethane, tetrachloroethylene, chlorobenzene, 1,1,2,2- tetrachloroethane, 4-chlorotoluene, 1,4-dichlorobenzene, 1,2-dichloropropane, 1,1,2-trichloroethane, 1,2-dibromoethane, 1,2,3-trichloropropane and hexachlorobutadiene. Mean percentage recoveries, using 2.0 mL DMSO per elution, ranged from 74 to 103 percent with these mixtures. While most experiments utilized a one litre spiked sample, the method was also found applicable to larger sample volumes. Four litres (spiked at 0.25 mg/L) were concentrated sequentially to 4.0 mL by the two-trap system with a mean recovery efficiency of close to 100 per cent.

The DMSO, being of intermediate volatility, had a solvent peak which interfered chromatographically with the identification of certain compounds. It was determined that methanol provided equivalent elution efficiency and was also a suitable solvent for mutagenicity testing. This is recommended as an alternative solvent if subsequent identification of components becomes necessary.

The concentration technique described has been successfully applied to environmental samples and has been integrated into the mutagenicity testing program for industrial effluents in the Province of Ontario.

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CONTROLLED POTENTIAL COULOMETRIC ANALYSIS OF HEAVY METALS

Controlled potential coulometry (CPC) is an "absolute" technique which makes it ideally suited for the assay of primary standards, while its sensitivity, accuracy and ease of operation makes it an excellent choice for environmental analysis.

The technique of CPC involves exhaustive electrolysis of a solution at an electrode set at constant potential and concomitant time integration of the electrolysis current.

The electroactive species in solution is depleted during the course of the electrolysis and the accumulated charge at the end of the electrolysis is directly related to the weight of the electroactive species, as defined by Faraday's Law of Electrolysis. Faraday's Law states that the total chemical change produced at the electrodes of a cell is directly related to the quantity of electricity in coulombs passed through them.

$Q = FWn/M$ where Q = charge accumulated during electrolysis, F (Faraday) = 96,487 coulombs/gram equivalent weight of electrochemical charge, W = Weight of electroactive species in grams, M = Gram molecular weight of electroactive species, n = number of electrons exchanged per atom of electroactive species.

For analytical purposes this equation is rearranged to solve for W, since F, n, and M are constants and the value of Q can be determined experimentally.

As an example, the CPC of a solution containing 1 mg Cu^{+2} would yield

$$Q = 96,487 \times 10^{-3} \times 2/63.54$$
$$= 3.037 \text{ Coulombs}$$

The direct relationship between Q and W obviates the need for calibration curves, standard solutions, end-point detectors, etc. CPC is one of the most accurate and precise methods for the analysis of heavy metals. Routine analyses can be completed in a matter of minutes. It can be applied to the analysis of electroactive species present at levels down to parts per million.

Controlled Potential Coulometric Analysis of Metal Stock Solns.

Element	Av. Wt. Taken (mg)	Av. Wt. Found (mg)	Mean Deviation %
Cu^{+2}	1.0	1.0011	.11
Cr^{+6}	1.0	1.0009	.09
Mn^{+2}	1.0	1.0150	1.50
Fe^{+2}	1.0	0.9884	-1.18
Cd^{+2}	1.0	1.0020	.20
Pb^{+2}	1.0	1.0090	.90

1 ml of 1000 ppm stock solution aliquot was taken for each analysis. Result stated is the average of 3 tests.

The technique of CPC has been evaluated with a number of stock standard solutions. The results for the analyses of Cu^{+2}, Cr^{+6},

Mn^{+2}, Fe^{+2}, Cd^{+2}, Pb^{+2} in stock standard solutions are shown in the table. The accuracy and precision achieved with the technique are illustrated by the data. CPC can be applied for the determination of more than 30 elements.

The technique of CPC can be applied in certification of standards, which are used in analytical procedures for court cases, and also in ongoing laboratory quality control procedures. The technique can also be used to determine the oxidation states of metal ions in a given solution, for example, As^{+3}/As^{+5}, Fe^{+2}/Fe^{+3}, U^{+4}/U^{+6} and Cr^{+3}/Cr^{+6} ratios in natural waters and sediment leachates. The application of CPC to some types of environmental analysis will represent significant progress, but the real benefit of the technique lies in the provision of a precise, rapid means of certifying the stock standard solutions that are the cornerstones of accurate analytical methodologies.

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AIR POLLUTION INDICATORS USING COEFFICIENT OF HAZE TAPE SAMPLERS

The Ministry of the Environment operates coefficient of haze (COH) samplers at all major areas within the Province to continuously determine the soiling properties of atmospheric dust. The method is based on the filtration of airborne dust through a paper tape and the measurement by light transmittance of the extent of soiling or darkening of clear filter paper. The sampling paper is normally Whatman 41 cellulose paper, 1½" wide in 50' rolls, and one roll can last for over three weeks. The sampler can be operated for periods of 1, 2 or 4 hours at an air flow of 0.4 m³/hr.

The standard high volume (Hi-Vol) air samplers operate over a 24-hour period and thus can only provide an average pollutant value for the exposure period. Weather and emission conditions can change dramatically over that period and the time when these changes occur cannot be determined using a Hi-Vol sampler. Analysis of exposed COH tapes can produce an hourly differentiation of pollutant levels for the period of investigation. The heavy metals that have been studied include lead, iron, copper and zinc.

Comparable COH and Hi-Vol sampler operating conditions are tabulated below:

Parameters	COH	Hi Vol
Flow m³/hr	0.4	83
Filter area cm²	5.1	407
Type of filter	Whatman 41	Glass fibre
Flow/unit filter area m³/hr	0.077	0.204

The disadvantages of the COH sampler are that the amount of material collected is small and that the Whatman 41 paper is only 60-70% as efficient as the glass fibre for removing particles down to 0.3 um in diameter. Glass fibre tape cannot be used in the COH unit since it is very fragile and contains high background levels of heavy metals. Because of these shortcomings, COH samplers cannot presently be used to determine absolute pollutant levels. However, they can provide valuable information on trends for individual air pollutants over a short time interval.

Because the air volumes are small, the amounts of particulate matter sampled are low, and thus the analytical methods applied require much greater sensitivity than for Hi-Vol analysis. Taking lead as an example, for rural areas the level ranges between 0.1-0.3 ug/m³ and for a downtown area 0.8-3.0 ug/m³. Thus the expected level of lead in the COH tape ranges from 0.07 to 2.3 ug compared to a Hi-Vol range of 200-6,000 ug.

Three analytical techniques are currently available which can attain the necessary sensitivity for metals analysis. They are:

a - ashing followed by digestion in nitric acid and determination by flameless or flame atomic absorption spectrophotometry,

b - ashing, HNO_3 digestion, followed by flame emission or inductively coupled plasma emission spectrometry,

c - x-ray fluorescence.

The limits of detection of these methods for lead are:

$$a - 0.02 \text{ ug/m}^3$$
$$b - 0.12 \text{ ug/m}^3$$
$$c - 0.8 \text{ ug/m}^3$$

Both methods a) and b) have the disadvantage of being time consuming and care has to be taken at the ashing stage to prevent loss of lead. X.R.F. is at least four times faster

than the other two methods and thus cost effective, but has a higher limit of detection. This level is only slightly greater than the normal background levels of lead in ambient air, thus only periods of high emission rates will be detected.

This technique has been applied to monitoring lead emissions from refiners and smelters, iron from steel works, coal from coal piles, changes in metal levels during periods of high pollution indices and the effect of vehicular traffic on lead levels near highways. For the study of lead smelters one unit was operated for several months and by relating wind direction and speed to lead loading on the tape, the Laboratory was able to provide data on emissions from various sections of the plant, times of high emissions and the contribution from highways and expressways. Currently two units are operating upwind and downwind of the plant and the plant contribution is being monitored.

This technique is being considered for a gravel quarry emission study and as an in-stack monitor for lead.

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ASSOCIATION OF COTTAGE-DEVELOPED SHORELINE WITH BACTERIAL POLLUTION OF WATER IN RECREATIONAL LAKES

As part of the Recreational Lakes Pollution Control Program, microbiological surveys have been carried out on about 90 lakes in Ontario. Although water quality was generally very good, low levels of fecal pollution were detected in localized areas of many lakes.

A recent review of this data for lakes in Muskoka has shed light on the origin and significance of this pollution. Analysis of variance of a series of daily bacterial densities for all sampling locations was used to identify locations where bacterial densities were significantly higher than those of the main body of water. Assuming that such locations indicated an input of fecal bacteria, it was found that fecal pollution was more frequently associated with the cottaged shoreline (see table).

Although the lack of a methodology does not permit tracing the source of pollution directly to underground leakage of wastes from defective septic systems in the immediate area, increased densities of fecal coliform bacteria have been associated within localized shoreline areas to flooded and substandard septic tank-tile beds. Certain lakes have shown significant reductions in fecal coliform densities, suggesting that a program of septic tank-tile field improvements has been effective.

Further study showed temporary increases in densities following rainfall. This rainfall effect is more often associated with cottaged lakes. In one such study, which compared cottaged and uncottaged lakes 0.8 Km apart, a prominant "rainfall" effect was noted for the cottaged lake even though no serious septic system deficiencies could be detected in the area using the existing techniques.

The densities of fecal coliforms at these polluted shoreline locations ranged from a geometric mean of 3 to 18 FC/100 mL.

These appear to be safe when compared to the MOE guideline of 100 FC/100 mL which is based on large population studies. However, the potential hazard of leaching from septic systems lies in the localization of disease organisms which can occur if the users of the waste disposal system are in fact disease carriers. The data from these studies tends to confirm the value of the MOE guidelines for septic system installations in maintaining or improving lake water quality and reducing local health hazards.

	TYPE OF SHORELINE	
	Cottaged	Un cottaged
Locations with Fecal Pollution	21	3
Pollution-Free Locations	566	431
Frequency (%) of Pollution at Shoreline Locations	3.57	0.69

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DATA QUALITY: LOOKING TO THE FUTURE

The past few years have seen the terms "quality assurance" and "quality control" introduced into every field of human endeavour. This is partially in recognition of the fact that it has become possible for a system to "function" and yet not "produce", partially because we have gained a better understanding of how product quality can be monitored and thereby improved, and partially because of a gut feeling that things don't work as well as they did, when individual craftsmen stood behind their product.

There are those who believe that no one cares anymore, but is this really true? Is it not more likely that society's needs for quality, and the complexity of the product, have surpassed the capability of the individual to meet these demands? Many tasks now require the joint effort of many individuals who work in isolation and who no longer can perceive or appreciate their role within the overall task. Certainly the automation, which has accompanied industrialization, has provided increased control over the mechanical (non-human) aspects of our daily tasks, but at the same time it has seemed to decrease the skill required of the human operator, and thus his interest in the job. Of course there are skilled, specially trained or inventive, individuals whose purpose it is to "keep the wheels turning", but more and more these people are divorced from reality, i.e. they don't have to know, nor are they necessarily required to know, why the wheels are turning.

Until very recently neither the understanding nor the technology existed to develop the type of data base required to investigate the natural variability of our enviornment. Trace materials could not be detected by the classical analytical techniques available. Methods used were insensitive, labour-intensive, and of unknown or undetermined accuracy. Changes in analytical technique used would mask the natural variability of background levels of environmental constituents.

Fortunately, just as the quality of our environment began to visibly deteriorate, advances in technology began to provide us with tools more capable of monitoring it. However, in the interim, in order to correct the more obvious sources of pollution, engineering programs were initiated to construct abatement facilities. The costs of implementing such programs were usually borne by the polluter, and these were resisted through court actions. Initially this battle between the engineers in government and industry was readily resolved by presenting evidence of gross pollution, easily traceable to and identifiable as a product of certain industrial operations. As the major air pollutants have been reduced, however, advances in technology and human understanding have revealed that many industrial materials, when allowed to escape into the environment, can have significant deleterious effects even at trace levels. Increasingly, the chemical, physical and medical sciences have been pulled into the fray to assess these effects in order to assist the judiciary in resolving the issues and penalties. Data quality is an increasingly important factor.

The data produced more than five to ten years ago is becoming more suspect with each passing day. This does not mean that it was poor quality data back then. If any mistake was made, it was in failing to foresee that the data might be used in the future for a different purpose, and in failing to take all steps possible to maximize data quality. In the past two decades, we have moved from a state where sampling and testing programs were required to produce only rough estimates of the concentrations of major elements, to one where very precise and accurate measurements of properly identified ultratrace metals and organics are essential. Whereas previously these materials were only measured in the context of wastewater treatment, now they are monitored in an infinite variety of natural environmental samples.

Tracing the path of these micro-pollutants through the environment back to their source has placed an enormous strain on our analytical capabilities. Our inability to meet the need, has forced us to reinvestigate, and correct for, effects previously considered to be insignificant. Sample preservation, sources of container and reagent contamination, background levels of elements in the laboratory environment which may surpass those found in nature, the maintenance of labware and equipment, and the proper cleaning and use of sampling tools, and may other factors, have all become critical in ensuring data quality.

The assurance of data quality cannot be achieved by looking for simple answers to analytical problems, or by deleting certain precautionary activities because it is thought that some factors are less significant than

others. There was a time when the "system" could demand that only certain "standard" methods be used, (there weren't any others); when the quality of the result didn't matter as long as it was below some "action" level; when long term health effects were something one lived with. There was a time when data reported as lower than the analytical method could detect implied a safe situation; when analytical chemists could be content using insensitive techniques; when unsophisticated sampling procedures were adequate. Those days are no more.

Now we all must work together to determine what activities must be carefully controlled to ensure data of sufficient quality to at least partially withstand the probable advances to be made in technology and general data quality in the future. We must not make the same mistake again. We must look to the future.

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QUALITY ASSURANCE: CHANGING GOALS

When one thinks of data quality it is often put in terms of the analyst's capability to apply a predetermined analytical procedure in a way which will produce precise (repeatable) and accurate (free of error) results. This is only possible if well-defined techniques are applied in a controlled fashion. Thus emphasis has been placed on the use of quality control processes which will monitor and provide a continuing record of process quality and hence, it is assumed, data quality.

Nowadays, emphasis is being placed increasingly on the role of the program manager in defining program needs in such a way that the most cost-effective analytical method can be used. Management, as stated in a recent review of the U.S. EPA quality assurance program, has the prime responsibility for setting the monitoring objectives. Difficulties arise when data collected for one purpose are indiscriminately used for others, without making adjustment for the quality of the data relative to the raw needs.

It has been frequently stated that data of unknown quality are worse than no data at all since it could result in unnecessary and costly compliance programs. It must be recognized that "unknown quality" is not necessarily the result of poor analytical practice. The design and coordination of field sampling practices, shipping and preservation procedures and even the characteristics of the sample container can introduce sufficient change in the sample composition, that even the best, most controlled, analyst will produce the wrong result relative to the original sample content. It is concern for, and monitoring of, all these factors that constitutes a good quality assurance program.

There are significant differences between the U.S. EPA and the Ontario Ministry of the Environment (MOE) quality assurance programs, both in philosophy and implementation. Some of these result from the sheer magnitude of the task in the U.S. where a multitude of federal, state, university, private, industrial and commercial laboratories participate in pollution control monitoring and analytical activity. In the U.S. a great deal of work is contracted out. This creates a need for a bureaucratic, legislated approach to quality assurance, which includes laboratory certification and specification of analytical method and qualtiy control procedures. While this ensures that the worst situations are corrected, it does not always encourage excellence, since it is only human nature to do the minimum required.

In Ontario, where essentially all analytical needs for Ministry programs are met by the central and three regional provincial laboratories, it is easier to set and maintain a common standard of service.

The large diverse workloads create a routine approach to analytical service which, in order to meet the more stringent needs of certain programs, means often that data quality exceeds the current perceived needs of most field programs. In this environment, quality assurance endeavours to determine the ultimate performance of a method relative to the day-to-day routine which, as stated, often already provides better than acceptable data quality. Continuing investigations to determine those factors which degrade performance relative to the optimal results in continuing upgrading of data quality. Since these studies are carried out by the analyst in the course of his routine work, his studies and conclusions are based on data produced on a wide variety of samples analysed under routine conditions. Data can be obtained under parallel operating conditions over significant periods of time.

In this environment the analyst amasses

considerable experience which can be of inestimable value to the program manager in setting program objectives and directing appropriate control activity in the field. Thus, finally, we come the full circle of quality assurance, the best method available, run by trained staff, to meet or exceed specified program needs, based on knowledge gained from past experience under controlled conditions, which produces data good enough to direct future improvement in both field and laboratory performance.

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The chymists are a strange class of mortals, impelled by an almost insane impulse to seek their pleasure among smoke and vapour, soot and flame, poisons and poverty, yet among all these evils I seem to live so sweetly, that may I die if I would change places with the Persian King.

Johann Joachim Becher "Acta Laboratorii Chymica Monacensis, seu Physica Subterranea" (1669)

LABORATORY SERVICES BRANCH

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